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Relaxation Analysis of Electrode Crystal Materials for Secondary Lithium Ion Batteries

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Abstract

Relaxation analysis, I have invented first in the world, makes transition of electrode material from kinetic state to equilibrium state clear. I would like to introduce the relaxation analysis for some electrode materials here, and make discussions about the behavior of Li ion and the crystal structure of the electrode material.

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Keywords: Li ion; Electrode Material; Kinetic state; Equilibrium state

1. Introduction

When lithium is inserted into γ -Fe₂O₃ electrochemically, prolonged potential change is observed after termination of the insertion (Fig.1). It is considered that this phenomenon reflects some continuing crystal structure change even after lithium insertion. We inserted lithium into γ -Fe₂O₃, then made the circuit open and analyzed the material. We named the analysis “Relaxation Analysis”, because material is analyzed at relaxation process. We are now applying relaxation analysis to so many materials such as γ -Fe₂O₃[1-3], LiFePO₄[4], LiMn₂O₄[5,6], Li_{4/3}Ti_{5/3}O₄[7], LiCoO₂[8], and so on.

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2. Experimental

We charged or discharged the cell electrochemically with electrode material. When the required conditions were attained, we opened the circuit and removed the working electrode from the cell immediately in a glove box to avoid the local cell action between the electrode material and the current collector or the supplemental conductor. Then, we obtained the sample for XRD measurement. XRD patterns were measured with various relaxation time. The XRD patterns were analyzed by the Rietveld method using RIEVEC program coded by T. Yao[9-10].

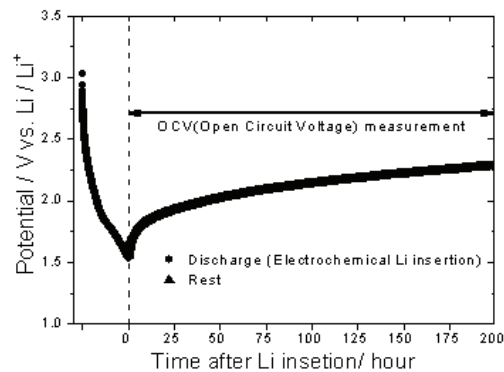


Fig. 1. Result of OCV (Open Circuit Voltage) measurement after lithium insertion (Sample : $\text{Li}_{1.5}\text{Fe}_2\text{O}_3$)

3. Results and Discussion

We measured crystal structure change of $\gamma\text{-Fe}_2\text{O}_3$ with spinel structure after termination of lithium insertion by using the X-ray Rietveld analysis and had a result that the iron occupancy of 8a site decreased and that of 16c site increased with lithium insertion process and after the lithium insertion, the iron occupancy of 8a site increased and that of 16c site decreased gradually at the relaxation process (Fig.2). And we concluded that this indicates that lithium prefer 8a site to occupy kinetically, on the other hand, prefer 16c site thermodynamically.

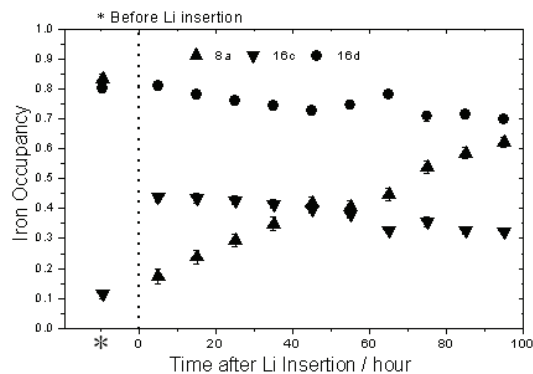


Fig. 2. Relaxation of crystal structure of $\gamma\text{-Fe}_2\text{O}_3$ with elapsed time after lithium insertion: Site occupancy changes of iron at 8a, 16c and 16d sites. Asterisk mark (*) indicates the sample before lithium insertion.

We analyzed the relaxation process of LiFePO_4 cathode after termination of lithium insertion by using X-ray diffraction measurement and the Rietveld analysis. It was found that the amount of LiFePO_4 decreased and that of FePO_4 increased after termination of the lithium insertion (Fig.3). It is considered that LiFePO_4 including lithium defects preferable for lithium diffusion formed during lithium insertion process and that the defective LiFePO_4 separated to LiFePO_4 without defects and FePO_4 at the relaxation process after the termination of lithium insertion.

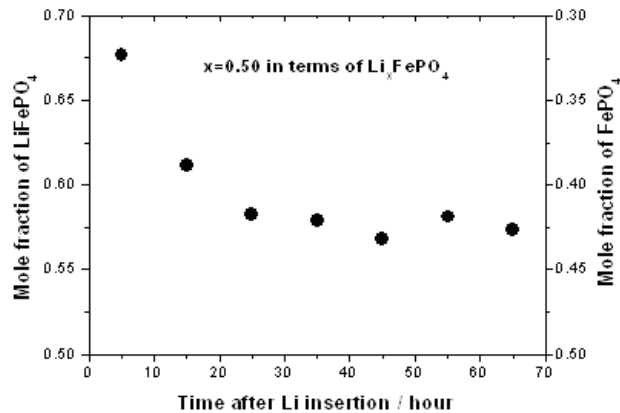


Fig. 3. The relative mol fraction changes of LiFePO_4 phase as a function of lithium insertion rate with various elapsed time after termination of lithium insertion process in the sample $x=0.5$ in terms of Li_xFePO_4 .

We measured phase change of LiMn_2O_4 after termination of lithium insertion. From the Rietveld analysis, it was found that the two phases, Li-rich phase and Li-lean phase, coexist and that the amount of Li-lean phase decreased and Li-rich phase increased with the various relaxation time (Fig.4). We considered that Li-lean phase has more defects than Li-rich phase and that Li-lean phase is kinetically favorable for Li to diffuse, and that, because Li-rich phase is thermodynamically more stable than Li-lean phase, Li-lean phase decreased and Li-rich phase increased at the relaxation process.

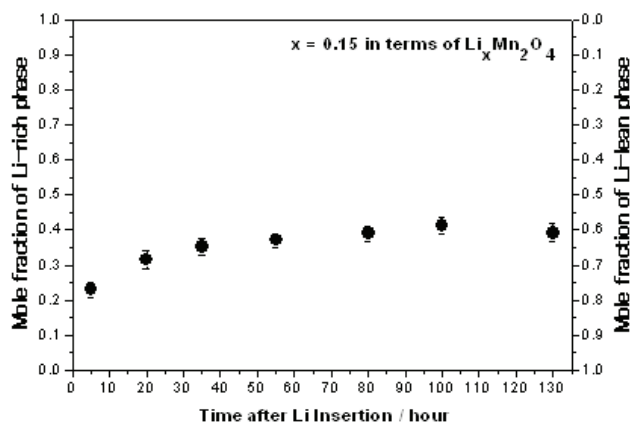


Fig. 4. The mol fraction change of Li-rich and Li-lean phase with the relaxation time in $\text{Li}_{0.15}\text{Mn}_2\text{O}_4$

4. Conclusion

I have presented dynamic changes in structures and/or phases of electrode materials according to the condition of Li transfer. Relaxation analysis will develop as the powerful method for analyzing electrode materials.

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